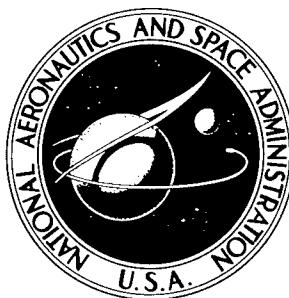


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COMPATIBILITY OF TANTALUM, COLUMBIUM, AND THEIR ALLOYS WITH HYDROGEN IN PRESENCE OF TEMPERATURE GRADIENT

by Joseph R. Stephens and Ralph G. Garlick

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SUMMARY

An investigation on the compatibility of tantalum and columbium with hydrogen in the presence of a temperature gradient was conducted to determine the suitability of these materials for use in a hydrogen-cooled nuclear rocket nozzle. Specimens having a temperature gradient from room temperature to approximately 3000° F were heated in a hydrogen atmosphere, held for a predetermined time, and cooled in hydrogen at rates from 25° to 1500° F per minute. Results showed that neither tantalum nor columbium is compatible with hydrogen under these conditions. A brittle hydride phase usually formed upon cooling below about 200° F in that portion of the specimen which had been held above about 1500° F. Hydrogen absorption and subsequent hydride formation in this part of the specimen is believed to be enhanced by removal of a surface oxide film during heating at elevated temperatures in hydrogen. Disintegration commonly accompanied formation of the hydride phase. Bend tests showed that hydrogen present in solution and as a hydride produced embrittlement and resulted in a ductile-brittle transition at room temperature for a hydrogen content as low as 2 atom percent (110 and 220 ppm by weight in tantalum and columbium, respectively).

Results also indicated that available commercial alloys of tantalum and columbium were not compatible with hydrogen under the imposed test conditions. An attempt was made to reduce the solubility of hydrogen in tantalum or columbium by alloying with rhenium to increase the electron-atom ratio. Results from tantalum-rhenium alloys indicated that at an electron-atom ratio of 5.5 (25 at. % Re) hydrogen absorption was reduced from 40.8 to 0.2 atomic percent for unalloyed and alloyed tantalum, respectively. At a corresponding electron-atom ratio a columbium-rhenium alloy absorbed 1.0 atomic percent hydrogen compared to 47.6 atomic percent hydrogen for unalloyed columbium.

It is concluded that unalloyed tantalum and columbium and their commercially available alloys are unattractive for use in hydrogen under conditions similar to those anticipated in nuclear rockets because of severe hydrogen absorption and embrittlement. 1 p 19

INTRODUCTION

Tantalum and columbium have been considered for use in portions of nuclear rocket reactors and rocket nozzles (ref. 1). In the nuclear rocket nozzle these metals in tubular form would be exposed to high-pressure hot hydrogen on one side and liquid hydrogen on the other, which would impose a temperature gradient from cryogenic to over 3000° F. For some proposed missions, the time of exposure would be of the order of 1 hour.

The purpose of this investigation was to assess the potential usefulness of tantalum and columbium in nuclear rocket applications, where they would be exposed to a hot hydrogen atmosphere for a relatively short time. Consideration of the tantalum-hydrogen and columbium-hydrogen phase diagrams, figure 1(a) (refs. 2 and 3) and figure 1(b) (refs. 2 and 4), suggests that, since the solubility of hydrogen is relatively low at high temperatures (above 1300° F) and since diffusion rates at lower temperatures are generally low,

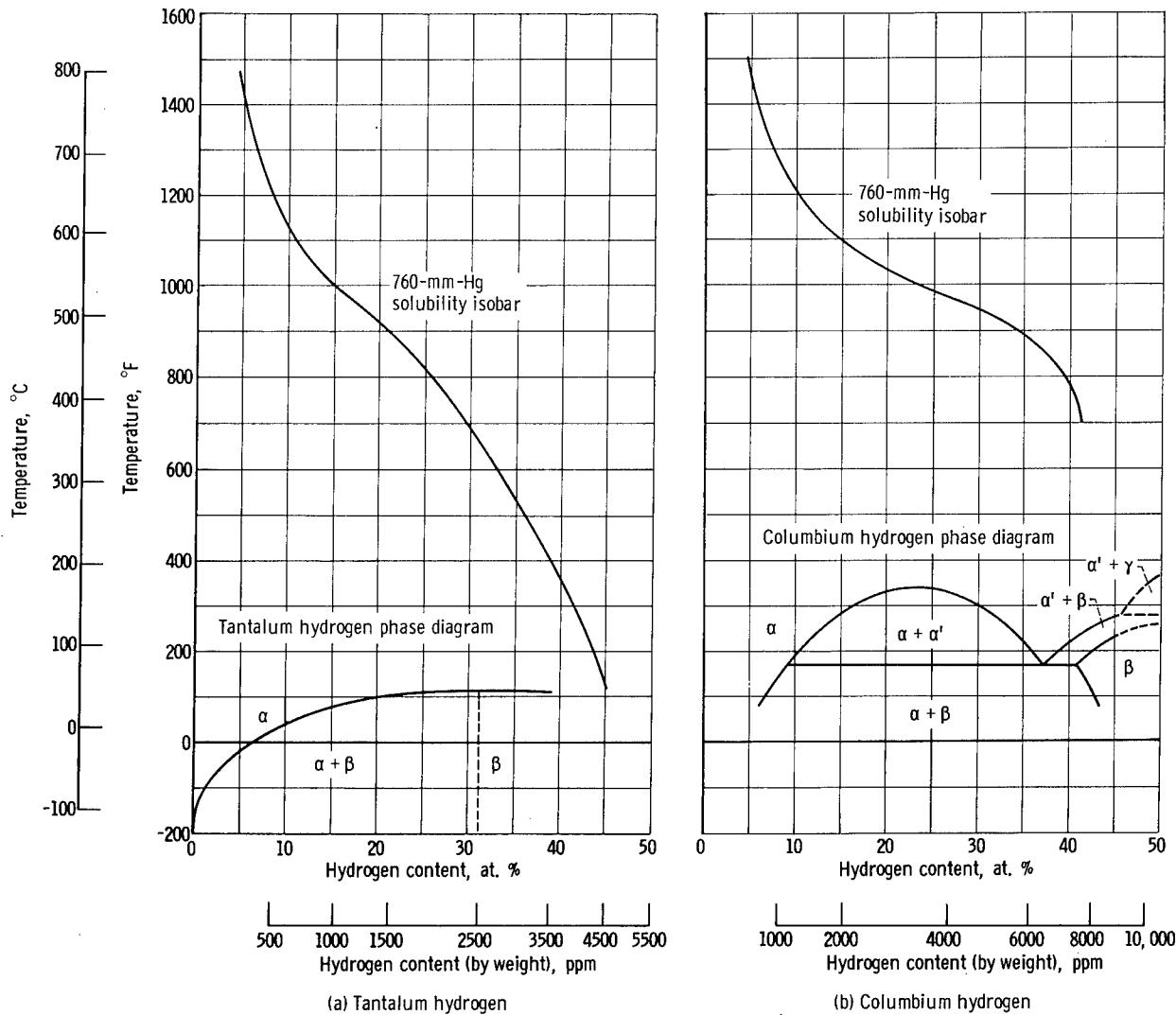


Figure 1. - Tantalum-hydrogen and columbium-hydrogen phase diagrams and solubility isobars (refs. 2 and 3).

it might be possible to use these metals in such short time applications.

Under nuclear rocket nozzle conditions, the effect of metal exposure to a temperature gradient in a hydrogen atmosphere cannot be simply predicted from phase diagrams and data on reaction kinetics because of factors such as thermal diffusion and absorption of hydrogen during cooling. This investigation was therefore conducted to determine the extent of deterioration resulting from exposure to a temperature gradient in a hydrogen atmosphere. Other factors such as heating rate, cooling rate, and exposure time also were studied.

Although it is known (refs. 5 and 6) that columbium and tantalum can be severely embrittled by hydrogen, the effects of a given concentration of hydrogen on the mechanical properties of these metals have not been well documented. A limited study of the effects of hydrogen concentration on ductile-brittle bend transition temperature of columbium and tantalum was included in this investigation.

A number of commercial tantalum and columbium alloys were screened to determine if any of these offered compatibility with hydrogen significantly improved over that of unalloyed columbium and tantalum. In addition, the possibility of reducing hydrogen solubility in tantalum and columbium by alloying with rhenium to increase the electron-atom ratio was briefly explored.

MATERIALS

Double-electron-beam melted tantalum and columbium were obtained as 0.025-inch sheet from commercial suppliers for this investigation. Chemical analyses of the unalloyed electron-beam-melted sheet are given in table I. Analyses of the three commercial tanta-

TABLE I. - CHEMICAL ANALYSES OF TANTALUM

AND COLUMBIUM SHEET

Element	Type of analysis	Tantalum sheet	Columbium sheet
		Impurity, percent by weight	
Carbon	Combustion, conductometric	0.0014	0.0059
Oxygen	Vacuum fusion	.0027 to 0.0133	.0023
Nitrogen	Kjeldahl	.0023	.0074
Hydrogen	Vacuum fusion	.00028	.00046
Iron	Emission spectrography	(a)	.002
Molybdenum	Emission spectrography	.005 to 0.007	.002
Silicon	Emission spectrography	(a)	.04

^aNot detected.

TABLE II. - CHEMICAL ANALYSES OF COMMERCIAL ALLOY SHEET

(a) Tantalum alloys

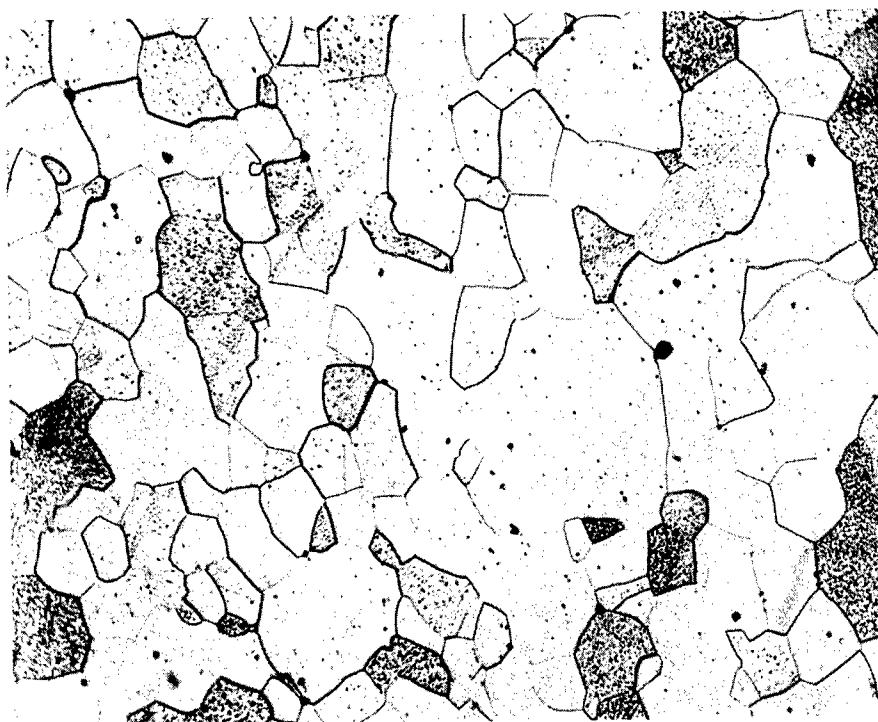
Alloy	Element content, percent by weight							
	Tungsten	Hafnium	Other	Oxygen	Nitrogen	Carbon	Hydrogen	Tantalum
Ta-10W	10.35	0.03	-----	0.0021	0.0040	0.0016	0.0001	Balance
T-111	7.60	2.36	-----	.0013	.0020	.0013	.0001	
T-222	9.11	1.91	-----	.0128	.0014	.0113	.0002	

(b) Columbium alloys

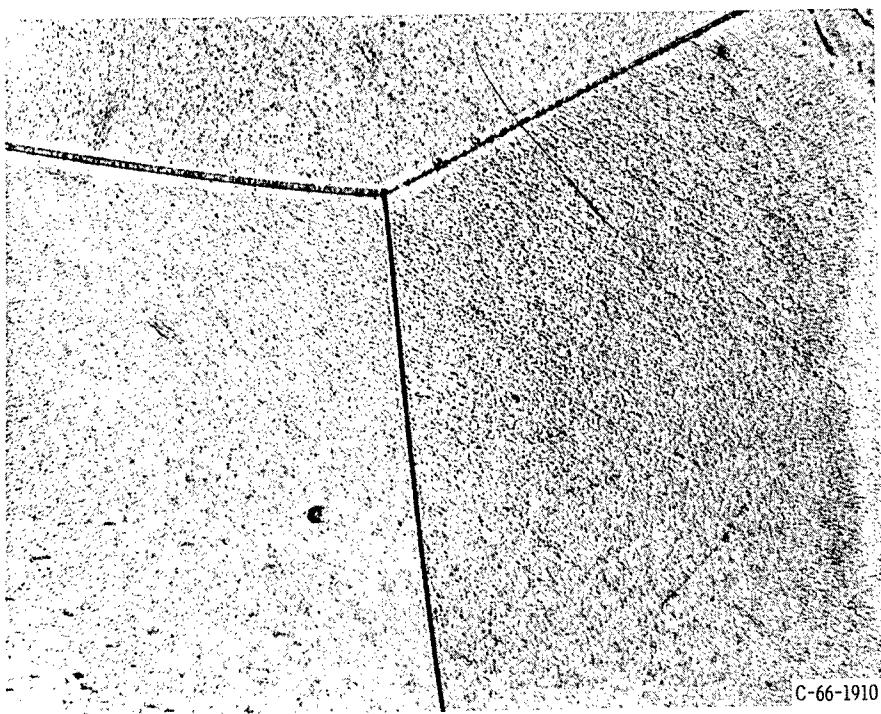
Alloy	Element content, percent by weight							
	Tungsten	Zirconium	Other	Oxygen	Nitrogen	Carbon	Hydrogen	Columbium
Cb-751	-----	0.95	-----	0.0073	0.0070	0.0100	0.0003	Balance
Cb-752	9.17	2.74	-----	.027	.0053	.0057	.0005	
D-14	-----	4.76	-----	.015	.0030	.0063	.0005	
AS-55	4.87	.91	Yttrium -0.39	.020	.0125	.059	.0001	
C-129	9.15	.67	Hafnium -9.18	.013	.0077	.0047	.0002	
FS-85	9.49	.80	Tantalum -27.8	.018	.0042	.0060	.0002	
B-66	-----	1.16	Molybde- num-4.85 Vanadium -5.02	.016	.0102	.0077	.0003	
D-43	9.05	1.04	-----	.0096	.0031	.086	.0001	
B-33	-----	-----	Vanadium -4.41	.055	.0086	.0120	.0003	
S-291	9.92	-----	Tantalum -9.81	.0127	.0028	.0060	.0001	

lum alloys and ten commercial columbium alloys which were investigated are listed in table II. The thickness of the alloy sheet ranged from 0.020 to 0.030 inch.

Alloys of tantalum plus 12.5, 25.0, and 37.5 atomic percent rhenium and columbium plus 15, 25, 35, and 40 atomic percent rhenium were prepared by pressing high-purity powders of these metals into 25-gram pellets. The alloys were consolidated by arc-melting the pellets with an inert electrode. The cast buttons were sectioned into approximately 0.25-inch cubes prior to testing in hydrogen. In addition to the buttons, a tantalum - 25 percent-rhenium alloy was cast into a 0.125- by 4.5-inch ingot and ground to 0.025 inch for temperature gradient testing.



(a) Tantalum.



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(b) Columbium.

Figure 2. - Microstructures of tantalum and columbium sheet. Annealed 1 hour at 3500° F. X250.

APPARATUS AND PROCEDURE

Temperature Gradient Tests

Specimens 0.5 by 4.5 inches were sheared from the 0.025-inch sheet of unalloyed tantalum and columbium for temperature gradient tests. In order to remove residual stresses and stabilize the grain size during subsequent testing, specimens were annealed for 1 hour at 3500° F in a vacuum of 8×10^{-6} torr. The specimens were fully recrystallized by this treatment as shown by the microstructures in figure 2.

The annealed specimens were tested (heated, held, and cooled) in a hydrogen atmosphere induction furnace as illustrated in figure 3. By heating 0.5 inch of the specimen within the susceptor and clamping 0.25 inch at the opposite end between water-cooled copper clamps, a temperature gradient from room temperature to 3000° F was established. The temperature distribution was determined by five thermocouples located as shown in figure 3. At maximum temperature during the test, a linear temperature gradient existed, typically from 500° F at a location 0.75 inch from the cold end to 3000° F at a location 0.0625 inch from the hot end. Hydrogen was passed through a dryer and purifier prior to entering the furnace at a flow rate of 25 cubic feet per hour. Analyses of the gas indicated that oxygen and water vapor were present in amounts totaling less than 20 parts per million. After heating for a predetermined time, specimens were cooled in hydrogen, at rates ranging from 25° to 1500° F per minute. Hydrogen contents of the specimens were

then determined by standard vacuum fusion techniques. The specimens were further evaluated by determination of hardness along the length of the specimens, metallographic examination, X-ray analyses of phases present, and qualitative description of the extent of reaction with tantalum and columbium as determined by disintegration of the test specimens.

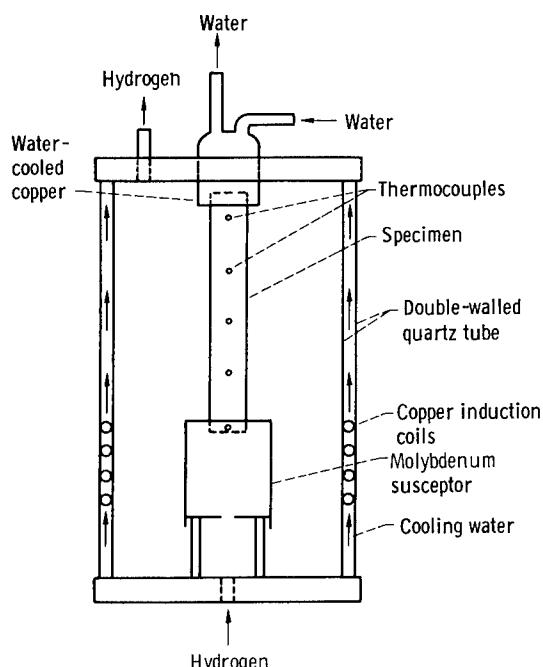


Figure 3. - Induction furnace for temperature gradient specimens.

Bend Tests

Longitudinal bend test specimens 0.025- by 0.5- by 1.25-inches were sheared from the unalloyed tantalum and columbium sheet and vacuum annealed as described previously. The specimens were then heated in hydrogen at 2000° F for 1 hour to remove any surface oxide and cooled to temperatures selected from the tantalum-

hydrogen and columbium-hydrogen phase diagrams and held at these temperatures for a minimum of 1 hour to ensure a uniform hydrogen concentration. In these particular tests, subsequent to hydrogen equilibration at the selected temperatures, hydrogen flow to the furnace was stopped and helium introduced to purge the system of hydrogen and to permit cooling in helium. This was done to prevent additional hydrogen absorption upon cooling.

A 4T bend test was used for ductile-brittle transition temperature determinations. The ductile-brittle bend transition temperature was arbitrarily defined as the minimum temperature at which specimens could be bent 120° over a 4T bend radius without fracture. Test conditions included a crosshead speed of 1 inch per minute, a span of 1 inch, and 0.1875-inch-diameter rollers as loading supports. A liquid-nitrogen apparatus similar to that described by Wessel (ref. 7) was used to obtain test temperatures below room temperature. A resistance-heated tube furnace was employed for tests above room temperature.

Alloy Specimens

The commercial tantalum and columbium alloys evaluated are listed in table II. Specimens 0.5 by 0.25 by 0.020 to 0.030 inch were heated to 3000° F in hydrogen, held for 1 hour and subsequently cooled to room temperature in hydrogen at a rate of approximately 1500° F per minute. Based on results of temperature gradient tests for unalloyed tantalum and columbium, this treatment was selected to assess the compatibility of the alloys with hydrogen. Alloy specimens were qualitatively evaluated by determining their room temperature ductility and extent of deterioration after heating in hydrogen. In addition, two tantalum alloy specimens (tantalum - 10 percent tungsten and tantalum - 8 percent tungsten - 2 percent hafnium) 0.5 by 4.5 by 0.030 inch were heated in a temperature gradient from room temperature to approximately 3000° F and subsequently evaluated by determining the extent of hydrogen absorption and disintegration.

Tantalum-rhenium and columbium-rhenium buttons were sectioned into approximately 0.25-inch cubes and heated in hydrogen at a constant temperature of 3000° F for 1 hour. These were cooled in hydrogen at a rate of 1500° F per minute to room temperature and analyzed for hydrogen. Tantalum and columbium 0.25-inch cubes were also sectioned from cast buttons and heated under similar conditions for comparison with the alloys studied.

RESULTS AND DISCUSSION

Evaluation of Thermal Gradient Tests

Data from 23 temperature gradient tests for columbium, tantalum, and tantalum alloys are summarized in table III. Chemical analyses of sheet specimens from the thermal

TABLE III. - SUMMARY OF TEMPERATURE GRADIENT DATA

(a) Tantalum and tantalum alloys

Specimen	Approximate maximum temperature, °F	Atmosphere during heating	Heating rate, °F/min	Atmosphere at maximum temperature	Time at maximum temperature, hr	Atmosphere during cooling	Cooling rate, °F/min	Distance from cold end, in.						Appearance after treatment
								$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{1}{4}$	3	$3\frac{3}{4}$	$4\frac{1}{2}$	
Unalloyed tantalum														
3	3000	Hydrogen	100	Hydrogen	1	Hydrogen	400	---	1.8	---	3.1	---	3.9	Surface dull at 3 in.
4	3000	Hydrogen	100	Hydrogen	1	Hydrogen	40	---	6.1	11.7	---	---	^a 22.1	Disintegrated at $2\frac{1}{2}$ in.
5	3000	Hydrogen	40	Hydrogen	1	Hydrogen	400	---	2.9	4.9	7.9	11.7	13.8	Surface dull at 3 in.
6	3000	Argon	100	Hydrogen	1	Argon	400	---	.6	---	.3	---	.04	Clean surface
14	3000	Argon	100	Hydrogen	1	Argon	40	---	.2	---	.2	---	.1	Clean surface
101	3000	Hydrogen	75	Hydrogen	1	Hydrogen	50	5.0	6.0	7.9	11.3	15.6	24.2	Disintegrating at $4\frac{1}{4}$ in.
102	3000	Hydrogen	75	Hydrogen	1	Hydrogen	25	1.6	3.0	4.5	6.8	10.7	18.6	Disintegrating at 3 in. and at $4\frac{1}{4}$ in.
103	3000	Hydrogen	75	Hydrogen	1	Hydrogen	25	4.8	5.0	5.4	5.7	7.5	^a 6.4	Disintegrated at $3\frac{3}{4}$ in.
104	2000	Hydrogen	75	Hydrogen	1	Hydrogen	25	---	---	---	---	---	---	Disintegrated at $3\frac{3}{4}$ in.
105	3000	Hydrogen	75	Hydrogen	24	Hydrogen	1500	---	---	---	---	---	^a 22.6	Disintegrated at $2\frac{1}{2}$ in.
107	3000	Hydrogen	75	Hydrogen	4	Hydrogen	1500	5.3	6.3	7.5	8.3	---	---	Disintegrated at $3\frac{3}{4}$ in.
109	3000	Hydrogen	75	Hydrogen	4	Hydrogen	1500	.2	.2	7.2	7.2	---	^b 38.2	Discontinuous specimen
112	3600	Hydrogen	75	Hydrogen	.01	Hydrogen	1500	.04	.5	2.4	5.0	14.0	18.5	Clean surface brittle at hot end
90 Percent tantalum - 10 percent tungsten														
15	3000	Hydrogen	100	Hydrogen	1	Hydrogen	100	---	---	---	---	---	---	Disintegrated at $3\frac{1}{4}$ in.
90 Percent tantalum - 8 percent tungsten - 2 percent hafnium														
16	3000	Hydrogen	100	Hydrogen	1	Hydrogen	100	---	---	---	---	---	---	Disintegrated at 2 in.
75 Percent tantalum - 25 percent rhenium														
110	3000	Hydrogen	75	Hydrogen	1	Hydrogen	25	---	0.4	---	0.2	0.6	0.2	Clean surface

(b) Columbium

Specimen	Approximate maximum temperature, °F	Atmosphere during heating	Heating rate, °F/min	Atmosphere at maximum temperature	Time at maximum temperature, hr	Atmosphere during cooling	Cooling rate, °F/min	Distance from cold end, in.						Appearance after treatment
								$\frac{3}{4}$	$1\frac{1}{2}$	$2\frac{1}{4}$	3	$3\frac{3}{4}$	$4\frac{1}{2}$	
Hydrogen content, at. %														
1000	3000	Hydrogen	75	Hydrogen	1	Hydrogen	25	1.4	3.0	46.5	---	---	---	Disintegrated at $2\frac{1}{4}$ in.
1001	3000	Hydrogen	75	Hydrogen	1	Hydrogen	50	1.8	3.1	13.0	10.7	---	---	Disintegrated at $2\frac{3}{4}$ in.
1004	2350	Hydrogen	75	Hydrogen	.01	Hydrogen	1500	2.6	3.5	3.8	4.3	15.2	47.5	Disintegrated at 4 in.
1006	3000	Hydrogen	75	Hydrogen	1	Vacuum	1500	.3	3.9	5.1	1.4	1.4	.8	Clean surface
1007	3000	Hydrogen	75	Hydrogen	.01	Hydrogen	1500	.03	.08	1.2	^a 24.2	---	---	Disintegrated at $2\frac{1}{2}$ in.
1008	3000	Hydrogen	75	Hydrogen and helium ^c	^c 1.5	Helium	1500	.13	.6	.16	.07	.12	---	Clean surface

^aPiece analyzed had fallen from specimen into susceptor.^bPowder had fallen into susceptor.^c1 hr in hydrogen; 0.5 hr in helium at temperature.

gradient tests indicated that the hydrogen concentration was greatest in the portion of the specimen that had been heated to the highest temperature (2000° to 3000° F). Also, an increase of specimen time in hydrogen resulting either from slower heating or cooling rates or longer times at temperature resulted in an increase of hydrogen absorption. Upon cooling below 200° F in hydrogen, formation of either tantalum hydride or columbium hydride occurred in that portion of the temperature gradient specimens which had been heated above about 1500° F. Hydride formation resulted in disintegration of the specimens or severe embrittlement, as indicated by their fragility upon handling. It should be noted that cooling in hydrogen from 3000° F at rates up to 1500° F per minute did not suppress the absorption of hydrogen and accompanying embrittlement. Cooling in argon or helium, however, after holding at 3000° F in hydrogen prevented any subsequent absorption of hydrogen and yielded temperature gradient specimens with very low hydrogen content, as can be seen in table III for tantalum (specimens 6 and 14) and columbium (specimen 1008).

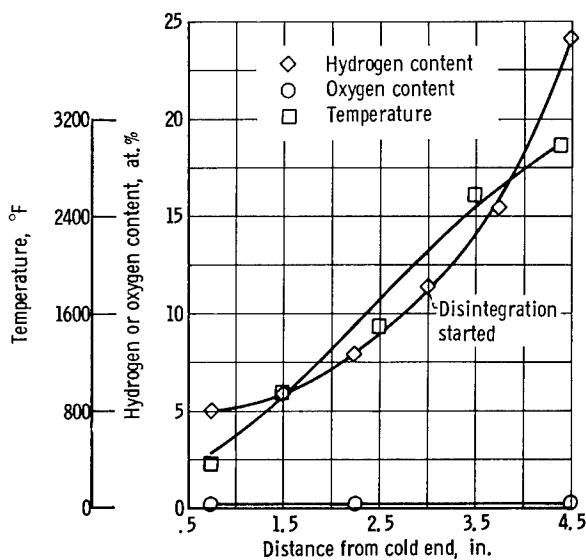


Figure 4. - Hydrogen content in tantalum temperature gradient specimen 101. Maximum temperature, 2980° F; time, 1 hour; heating rate, 70° F per minute; cooling rate, 40° F per minute.

Figure 4 illustrates a typical variation in hydrogen content along the length of a tantalum temperature gradient specimen. Oxygen content is also shown in the figure, and it can be seen that oxygen contamination was not excessive. As noted previously, disintegration of specimens upon cooling below 200° F occurred in the portion that had been heated to temperatures greater than 1500° F. The position where disintegration occurred in the specimen, 3 inches from the cold end, corresponds to a maximum temperature of 1850° F (fig. 4).

Figure 5 shows examples of specimens in the unexposed condition, after rapid cooling (400° F/min) from 3100° F (surface deterioration) and after slow cooling (40° F/min) from 2780° F (disintegration 3 in. from the cold end).

Absorption of hydrogen at the hot end of the specimen is unexpected since only small amounts should be absorbed at temperature, as illustrated by the tantalum-hydrogen phase diagram shown in figure 1(a) (p. 2). Also, rapid cooling would be expected to limit hydrogen absorption to small amounts. Results showed, however, that much higher cooling rates than 1500° F per minute would be required to suppress hydrogen absorption. Several investigations (refs. 6, 8, and 9) have indicated that hydrogen absorption is enhanced



(a) Unexposed specimen.



(b) Exposed to hydrogen atmosphere for 1 hour at 3100° F; heating rate, 40° F per minute; cooling rate, 400° F per minute.



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(c) Exposed to hydrogen atmosphere for 1 hour at 2780° F; heating rate, 100° F per minute; cooling rate, 40° F per minute.

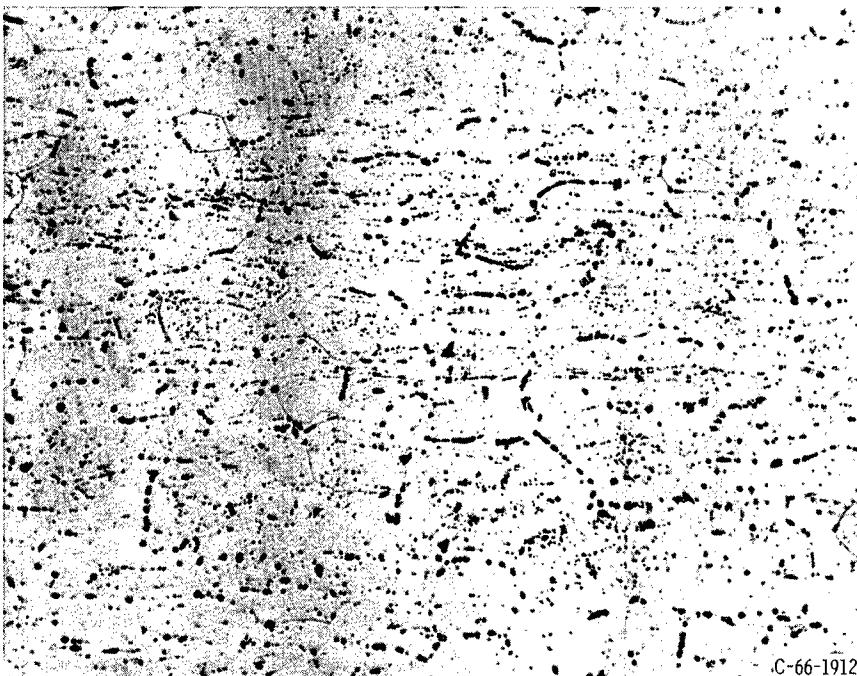
Figure 5. - Disintegration of tantalum temperature gradient specimen heated in hydrogen atmosphere. X1.4.

in columbium and tantalum by prior heating in hydrogen or thermal cycling in hydrogen to temperatures greater than 1650° F. This enhanced hydrogen absorption has been attributed to removal of a surface oxide film which retards hydrogen absorption (ref. 8). Thus, the activated surface resulting from heating to temperatures greater than 1650° F in hydrogen promotes hydrogen absorption during cooling. The observed variation in hydrogen content along the length of the temperature gradient specimens is consistent with this explanation, hydrogen absorption during cooling being high in the portion of the specimen that had been heated above about 1500° F. Because of the low solubility at high temperatures, only a small amount of hydrogen is absorbed until the specimen is cooled to lower temperatures, where the solubility is higher.

To test this hypothesis further, thermal gradient specimens of both tantalum and columbium were heated in hydrogen to 3000° F at a rate of 100° F per minute. Specimens were held in hydrogen at this temperature for 1 hour, and then hydrogen flow was stopped and helium was introduced into the furnace. After the specimen had been held in helium for 15 minutes at 3000° F, they were cooled in helium to 800° F, where helium flow was stopped. Hydrogen was reintroduced into the furnace and cooling continued to room temperature. During cooling in hydrogen from 800° F, the specimens disintegrated as a result of hydride formation. It should be noted that heating from room temperature to only



(a) 3.25 Inches from cold end; temperature, 2290° F.



(b) 4.125 Inches from cold end; temperature, 2980° F.

Figure 6. - Microstructures of tantalum temperature gradient specimen 101. X250.

800° F in hydrogen did not facilitate hydrogen absorption. Furthermore, cooling from 3000° F in helium prevented hydrogen absorption. From the tests described previously it is concluded that heating in hydrogen at 3000° F does facilitate removal of an oxide film on tantalum and columbium which impedes hydrogen absorption. Also, cooling in hydrogen is not required for low-temperature hydrogen absorption, if the oxide film has been removed. Rapid hydrogen absorption occurs at low temperatures after surface activation.

Metallographic studies verified that hydrogen content was greatest at the hot portion of the specimens. Photomicrographs of specimen 101 (hydrogen content shown in fig. 4) are shown in figure 6. At a distance of 3.25 inches from the cold end of the specimen (fig. 6(a)) second-phase particles are observed concentrated near the surface of the specimen. Figure 6(b), which is representative of the entire specimen thickness at this position, shows that the particles are uniformly distributed throughout the cross section of the specimen at a distance of 4.125 inches from the cold end. These structures are similar to the structure of tantalum hydride in tantalum shown by Wilcox (ref. 10). X-ray diffraction of sections of specimen 101 indicated that at a distance of 3.125 inches from the cold end tantalum and γ -tantalum hydride were present, while at a distance of 4.125 inches from the cold end only γ -tantalum hydride was detected. The analyzed hydrogen contents of 11.3 and 24.2 atomic percent (fig. 4) indicate the presence of some unhydrided tantalum at both positions. As noted in figure 4 the specimen contained cracks and had started to disintegrate at a point 3 inches from the cold end. The new surfaces exposed by cracks promote additional hydrogen absorption and disintegration of the specimen.

Hardening is normally associated with interstitial contamination. It can be seen in figure 7 for a typical thermal gradient specimen that hydrogen had only a minor effect on

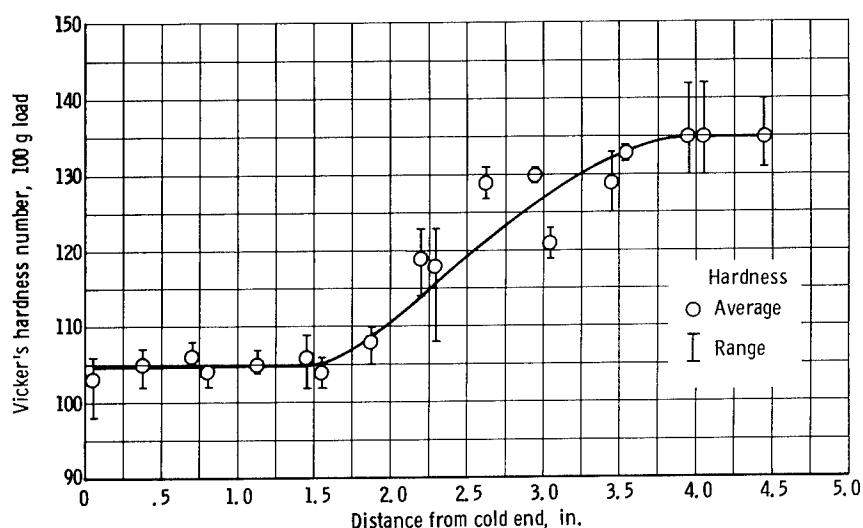


Figure 7. - Hardness of tantalum temperature gradient specimen 101. Maximum temperature, 2980° F; time, 1 hour.

the hardness of tantalum, since it produced an increase in hardness from a Vickers hardness number of 102 near the cold end to a Vickers hardness number of approximately 135 at the hot end. Corresponding hydrogen concentrations at these positions were 5.0 and 24.2 atomic percent, respectively.

In order to determine the role of thermal diffusion in the temperature gradient specimens, three tantalum specimens, each 1.25 inches long, were tied to a 4.5-inch-long molybdenum strip and heated in a temperature gradient. Alumina spacers prevented contact between the tantalum and molybdenum strip. The molybdenum strip and tantalum specimens were heated at a rate of 160° F per minute to a maximum temperature of 2800° F at the hot end, held for 4 hours, and rapidly cooled in hydrogen at a rate of approximately 1500° F per minute. Thermocouple readings indicated a linear temperature gradient along the molybdenum strip. Hydrogen content of the tantalum specimens is shown in figure 8.

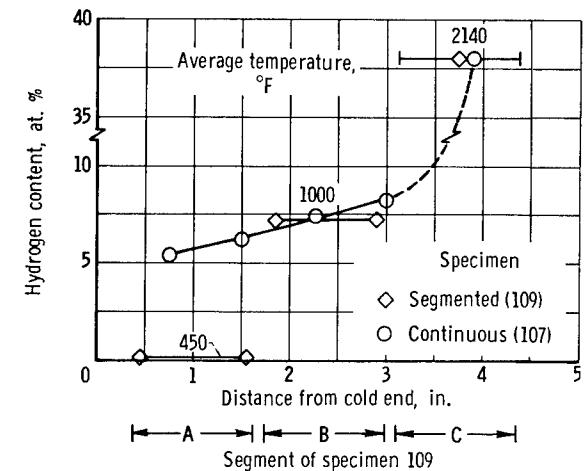


Figure 8. - Hydrogen content of tantalum temperature gradient specimens 107 and 109. Maximum temperature, 2800° F; time, 4 hours; heating rate, 160° F per minute; cooling rate, 1500° F per minute.

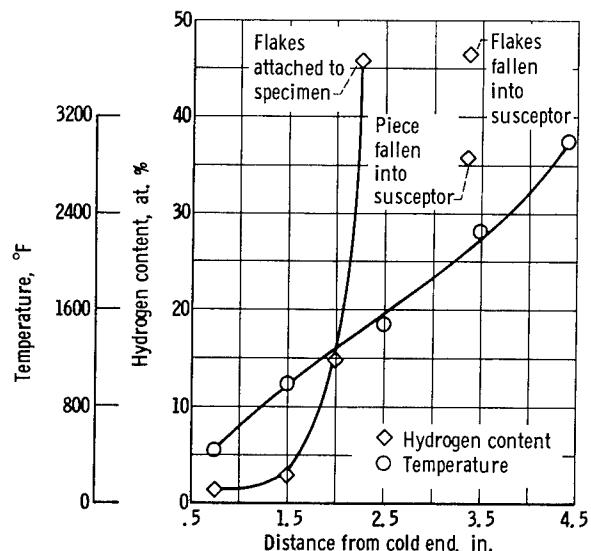


Figure 9. - Hydrogen content in columbium temperature gradient specimen 1000. Maximum temperature, 3000° F; time, 1 hour; heating rate, 70° F per minute; cooling rate, 25° F per minute.

Hydrogen analyses from each end of each of the specimens heated at 450° and 1000° F indicated uniform concentrations along the 1.25-inch lengths of 0.2 and 7.2 atomic percent hydrogen, respectively. The specimen heated at 2140° F disintegrated. Hydrogen analysis of the hydride flakes indicated 38.2 atomic percent hydrogen present. The apparent uniform hydrogen concentration in each segment suggests that the temperature was uniform throughout the length of each specimen.

These results are similar to those previously obtained on nonsegmented temperature gradient specimens heated under similar conditions, in that hydrogen absorption increased with increasing exposure temperature. The hydrogen contents of 38.2 atomic percent for the flakes and 7.2 atomic percent for the specimen heated at 1000° F agree with previous analyses, as shown in figure 8. The hydrogen content of 0.2 atomic percent for the specimen segment held at 450° F is much lower than that observed at the cool end of the con-

tinuous specimen (fig. 8). This suggests that diffusion of hydrogen may have occurred from the hot to the cold end of the nonsegmented temperature gradient specimens. Both tests show that hydrogen is absorbed at the surface activated portions of the specimens, i. e., after heating to higher temperatures in hydrogen.

Results for columbium were similar to those for tantalum. The reaction with hydrogen, however, appeared to be more severe for columbium than for tantalum. For example, columbium specimen 1000 in table III (p. 8) was heated in a manner similar to tantalum specimen 101 described previously. Disintegration occurred from a distance 2.25 inches from the cold end to the hot end of the columbium specimen. This is in contrast to the tantalum specimen, which remained intact although cracks formed approximately 3 inches from the cold end of the specimen. Hydrogen contents were determined on the solid 2.25-inch length of the columbium specimen 1000 and also on pieces of columbium and on hydride flakes that had fallen into the susceptor from the hot end of the specimen. As shown in figure 9, the hydrogen content increased rapidly beyond 2 inches from the cold end, which corresponds to a temperature of approximately 1250° F. The hydride flakes identified by X-ray diffraction as columbium hydride ($\text{CbH}_{0.89}$) had higher concentrations of hydrogen (47.5 at. %) than did pieces of columbium that had fallen into the susceptor from the hot portion of the specimen (35.9 at. %).

Because of severe embrittlement and disintegration of the columbium thermal gradient specimen heated at 3000° F, a second columbium specimen (1004) was heated to 2350° F for 2 minutes and cooled rapidly to room temperature in hydrogen. The second specimen still absorbed large amounts of hydrogen, as shown in figure 10. Hydride flakes formed at the hot end of the specimen upon cooling below 200° F. Hardness data are shown in figure 11 for the same specimen. As had been observed for tantalum, hydrogen had little effect on the hardness of columbium.

Photomicrographs of specimen 1004 are shown in figure 12. In figure 12(a), it can be seen that the growth direction of the hydride platelets changed at the grain boundary, which shows that in columbium the hydride precipitated on preferred planes. This type of hydride formation differs from the hydride precipitate observed in tantalum, where the second phase was globular. Figures 12(b) and (c) show the hydride needles and platelets occupying over half the specimen.

Ductile-Brittle Bend Transition Temperature Behavior

Bend specimens were heated to 2000° F in hydrogen and then held at some lower temperature, determined from the tantalum-hydrogen or columbium-hydrogen phase diagrams, to obtain a desired hydrogen content.

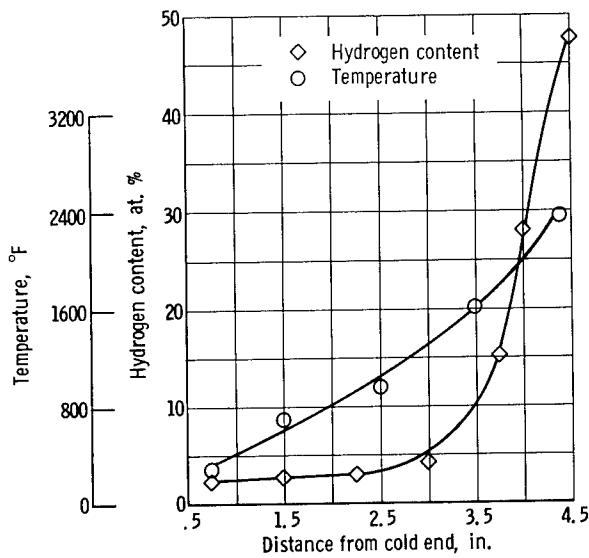


Figure 10. - Hydrogen content in columbium temperature gradient specimen 1004. Maximum temperature, 2350° F; time, 2 minutes; heating rate, 70° F per minute; cooling rate, approximately 1500° F per minute.

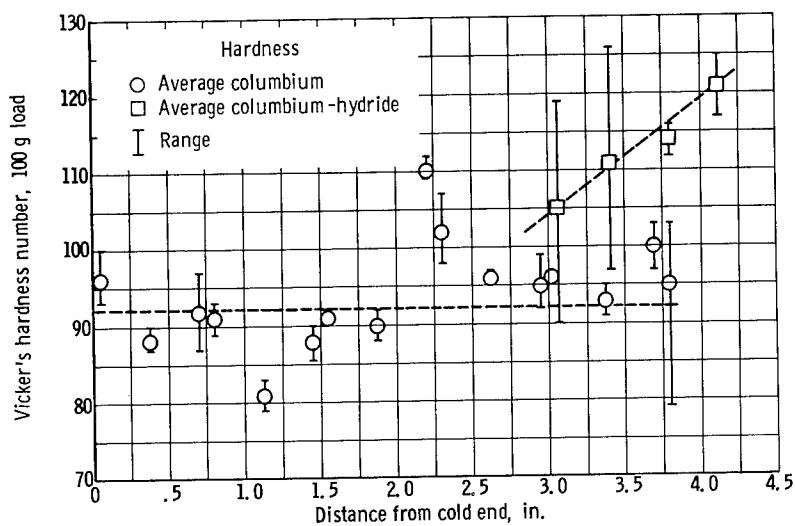
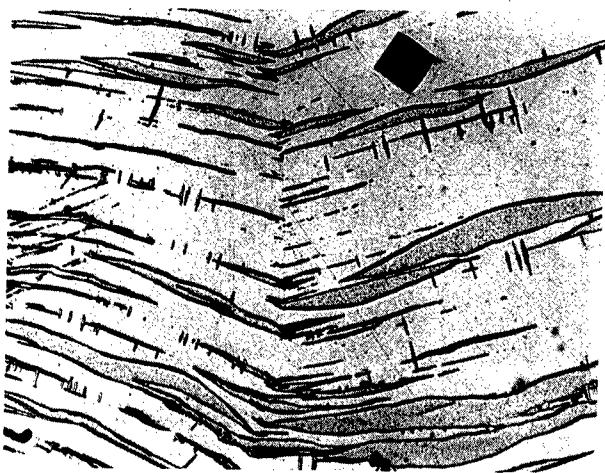
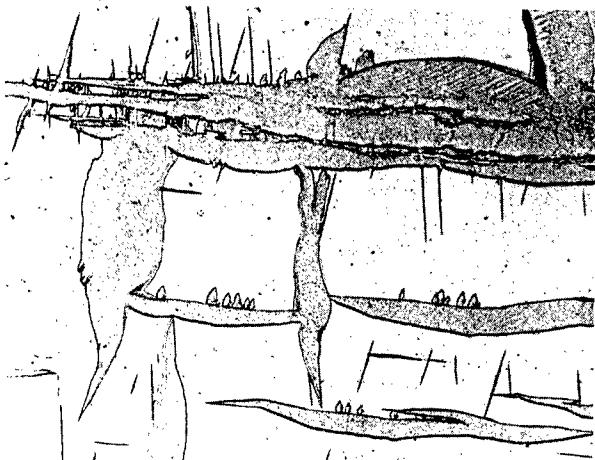


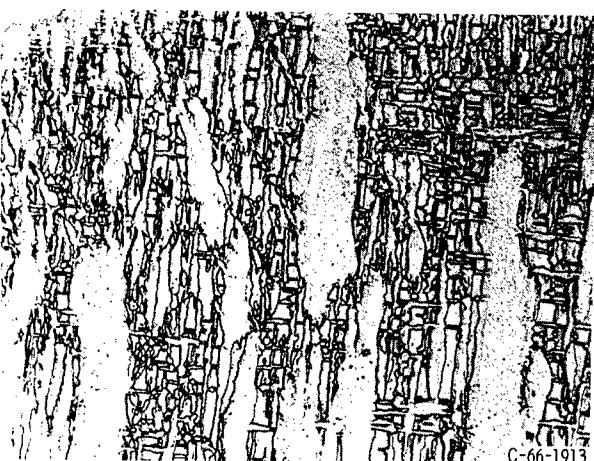
Figure 11. - Hardness of columbium temperature gradient specimen 1004. Maximum temperature, 2350° F; time, 2 minutes.



(a) 3.75 Inches from cold end. Hydrogen content, 15.0 atomic percent; temperature, 1860° F.

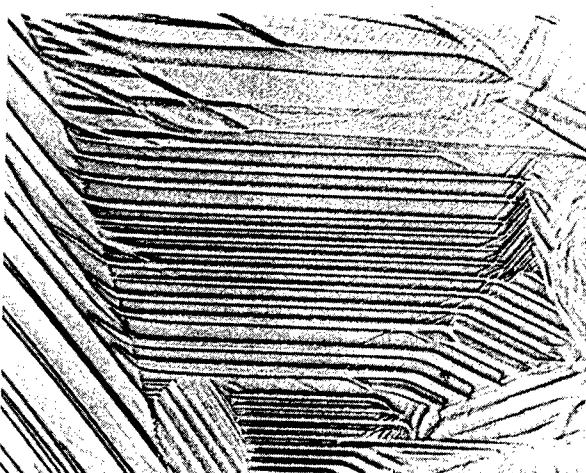


(b) 4.0 Inches from cold end. Hydrogen content, 28.0 atomic percent; temperature, 2070° F.

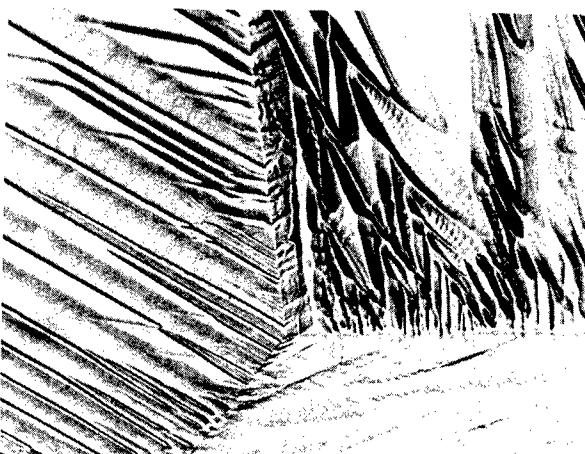


(c) 4.25 Inches from cold end. Hydrogen content, 39.5 atomic percent; temperature, 2260° F.

Figure 12. - Microstructures of columbium temperature gradient specimen 1004. Maximum temperature, 2350° F, time, 1 minute. X250. (Reduced 30 percent in printing.)



(a) Specimen 504; 38.0 atomic percent hydrogen. Equilibrating temperature 910° F. (Could not be tested.)



(b) Specimen 503; 34.4 atomic percent hydrogen. Transition temperature, greater than 1500° F; equilibrating temperature, 980° F.



(c) Specimen 502; 19.3 atomic percent hydrogen. Transition temperature, 375° F; equilibrating temperature, 1050° F.

Figure 13. - Microstructures of tantalum bend test specimens. X750. (Reduced 30 percent in printing.)

Tantalum specimens held at 390° F for 4 hours contained 38.0 atomic percent hydrogen and could not be handled without breakage. Specimens held at 570° F contained 34.4 atomic percent hydrogen and were brittle when bend tested at 1500° F . Microstructures of these specimens and additional specimens equilibrated in hydrogen at 750° F are shown in figure 13. Under these conditions precipitation occurred on crystallographic planes of the tantalum specimens. The second phase is unlike the hydride precipitate observed in temperature gradient specimens (fig. 6, p. 11), where globular precipitates were primarily along grain boundaries. X-ray diffraction data, however, indicated that both precipitates are γ tantalum hydride. A possible explanation for difference in hydride morphology is that temperature gradient specimens were cooled rapidly through the hydride formation temperature region. Hydrogen absorption may have been primarily along grain boundaries and thus lead to hydride precipitation in these areas. Bend test specimens

were held for 1 to 4 hours at temperature to allow hydrogen concentrations to reach equilibrium. A comparison of the tantalum-hydrogen phase diagram (fig. 1(a), p. 2) and the hydrogen contents of these three groups of specimens indicates that the expected hydrogen concentration was achieved for the two lower equilibrating temperatures. The acicular precipitates are apparently characteristic of the equilibrium condition.

The effect of hydrogen content on the ductile-brittle bend transition temperature of tantalum is shown in figure 14. It can be seen that 2 atomic percent (110 ppm by weight) hydrogen is sufficient to increase the transition temperature from $<-320^{\circ}\text{ F}$ for unalloyed tantalum to room temperature. This was a single-phased alloy in agreement with the phase diagram (fig. 1(a)).

Columbium bend test specimens were heated in a manner similar to the tantalum specimens to alloy with hydrogen. The columbium-hydrogen phase diagram (fig. 1(b)) was used to select the five annealing temperatures used. The effect of hydrogen content on the transition temperature of columbium is also shown in figure 14. It can be seen that approx-

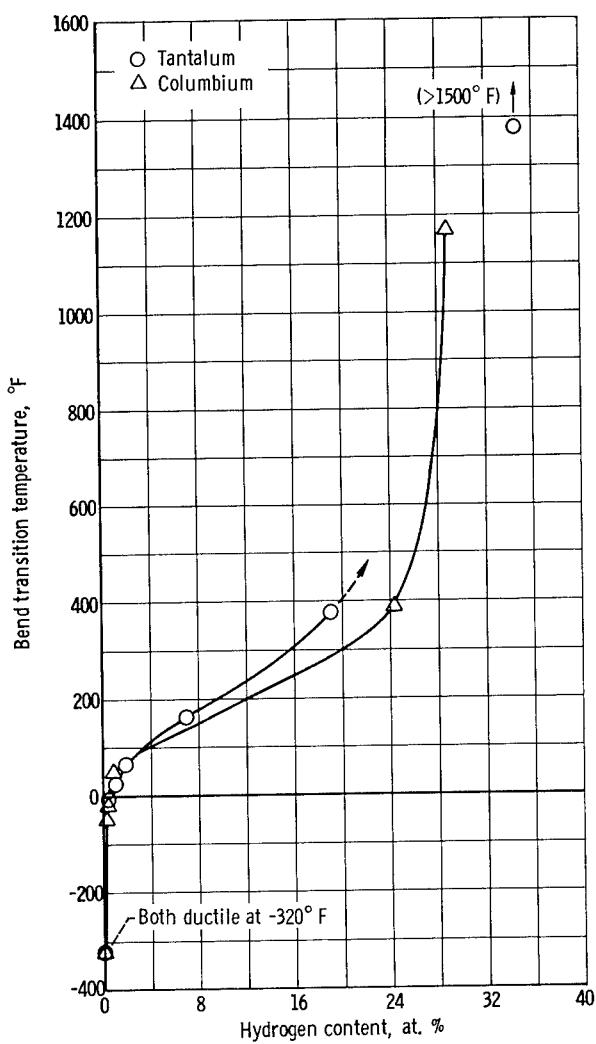
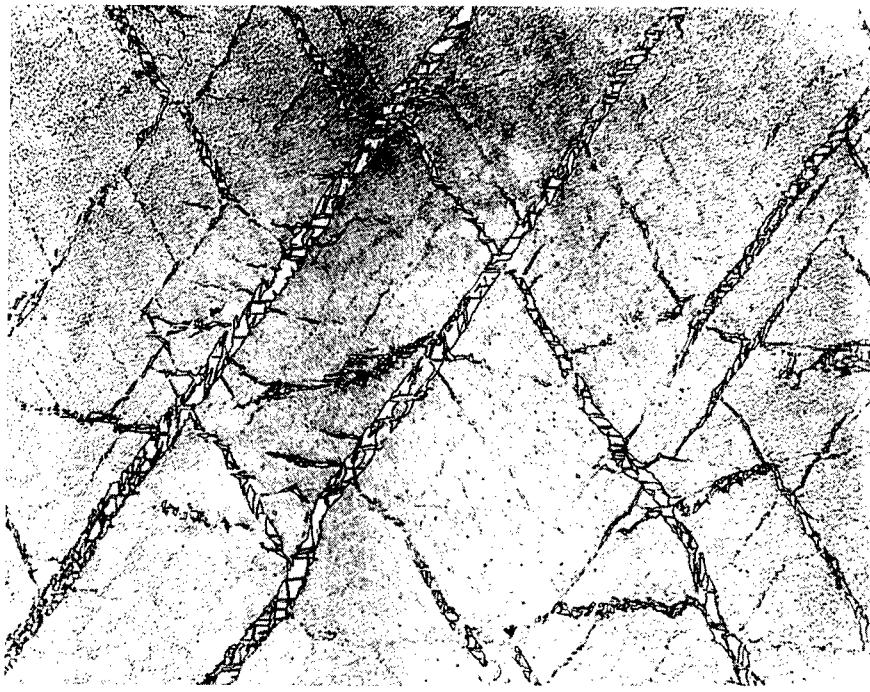
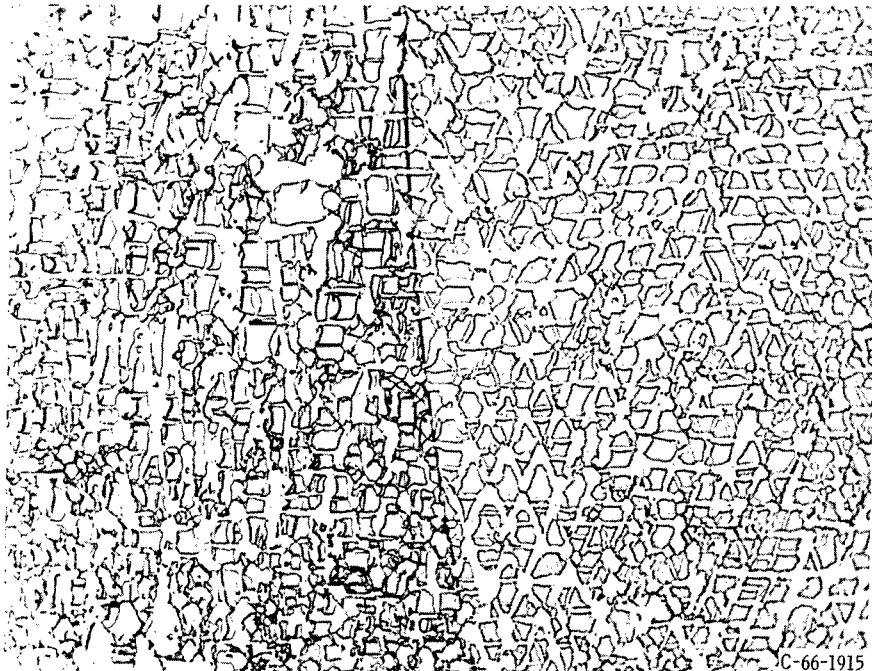


Figure 14. - Effect of hydrogen on ductile to brittle bend transition temperature of tantalum and columbium.



(a) Specimen 5005; 28.8 atomic percent hydrogen. Transition temperature, 1170° F; equilibrating temperature, 750° F.



(b) Specimen 5004; 24.5 atomic percent hydrogen. Transition temperature, 390° F; equilibrating temperature, 930° F.

Figure 15. - Microstructures of columbium bend test specimens. X750.

imately 2.0 atomic percent (220 ppm by weight) of hydrogen raises the transition temperature to room temperature, compared to $<-320^{\circ}\text{ F}$ for unalloyed columbium. Microstructures of bend test specimens containing 28.8 and 24.5 atomic percent hydrogen are shown in figure 15. The hydride precipitates are similar to those formed in the temperature gradient specimens (fig. 12). Both contain substantial amounts of hydride.

Alloy Studies

Table IV lists tantalum and columbium alloys that were evaluated by heating to 3000° F in hydrogen and gives a qualitative description of their appearance after this treatment. It is evident from these results that the alloys investigated are not compatible

TABLE IV. - COMPATIBILITY OF COMMERCIAL TANTALUM AND COLUMBIUM ALLOYS WITH HYDROGEN

[Specimens heated at 3000° F in hydrogen for 1 hr and cooled to room temperature in hydrogen atmosphere; cooling rate, $1500^{\circ}\text{ F/min.}$]

(a) Tantalum alloys

Alloy	Nominal composition, percent	Qualitative results
Ta 10 tungsten	10 Tungsten	Hydride flakes formed
T-111	8 Tungsten plus 2 hafnium	Hydride flakes formed
T-222	9.6 Tungsten plus 2.4 hafnium plus 0.01 carbon	Brittle at room temperature

(b) Columbium alloys

Alloy	Nominal composition, percent	Qualitative results
Cb - 751	1 Zirconium	Hydride flakes formed
Cb - 752	10 Tungsten plus 2.5 zirconium	
D - 14	5 Zirconium	
As - 55	5 Tungsten plus 1 zirconium plus 0.2 yttrium	
C - 129	10 Tungsten plus 10 hafnium	
FS - 85	28 Tantalum plus 10 tungsten plus 1 zirconium	
B - 66	5 Molybdenum plus 5 vanadium plus 1 zirconium	
D - 43	10 Tungsten plus 1 zirconium plus 0.1 carbon	
B - 33	5 Vanadium	Brittle at room temperature
S - 291	10 Tungsten plus 10 tantalum	Brittle at room temperature

TABLE V. - EFFECT OF RHENIUM CONTENT ON HYDROGEN
ABSORPTION IN TANTALUM-RHENIUM AND
COLUMBIUM-RHENIUM ALLOYS

[Specimens heated at 3000° F in hydrogen for 1 hr and cooled to room temperature in hydrogen atmosphere; cooling rate, 1500° F/min.]

(a) Tantalum alloys

Nominal rhenium content		Electron atom ratio	Hydrogen absorbed	
at. %	wt. %		ppm	at. %
0	0	5	3780	40.8
12.5	12.75	5.25	1860	25.3
25.0	25.5	5.5	11	.2
37.5	38.1	5.75	1	.018

(b) Columbium alloys

Nominal rhenium content		Electron atom ratio	Hydrogen absorbed	
at. %	wt. %		ppm	at. %
0	0	5	9100	47.4
15	26.2	5.3	3110	25
25	40	5.5	108	1.2
35	52	5.7	17	.2
40	57	5.8	6	.08

with hydrogen under the imposed conditions. These results were substantiated by heating tantalum - 10-percent-tungsten and tantalum - 8-percent-tungsten - 2-percent-hafnium specimens in a temperature gradient. Both specimens disintegrated at a distance 3 inches from the cold end after cooling below 200° F.

In view of the results of this investigation, an attempt was made to develop alloys of tantalum and of columbium with reduced hydrogen solubility. Robins (ref. 11) suggested that the solubility of hydrogen in the transition elements decreases with increasing electron-atom ratio. According to this hypothesis, alloying elements such as molybdenum, tungsten, rhenium, ruthenium, osmium, rhodium, and iridium should increase the electron-atom ratio of tantalum and columbium and reduce the hydrogen solubility. In order to assess the effect of an increased electron-atom ratio on hydrogen solubility, buttons of tantalum and columbium containing up to 40 atomic percent rhenium were prepared by arc-melting. Specimens cut from the buttons were heated for 1 hour at 3000° F and cooled slowly in hydrogen. Data on these alloys are given in table V, and a plot of hydrogen content as a function of electron-atom ratio is shown in figure 16. It can be seen from

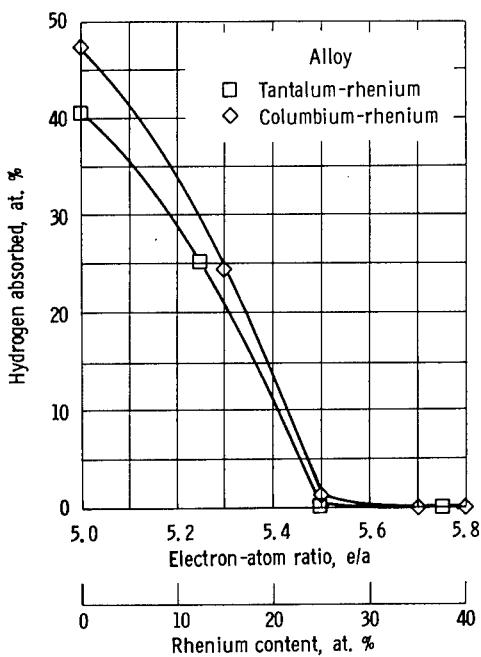


Figure 16. - Hydrogen absorption in tantalum-rhenium and columbium-rhenium alloys.

of rhenium additions are very encouraging from the viewpoint of hydrogen absorption, but fabricability decreases rapidly with increasing amounts of rhenium (ref. 13). However, in a recent investigation by Ritter, Geissen, and Grant (ref. 14) it was pointed out that columbium - 10 atomic percent rhodium or iridium (electron-atom ratio of 5.4) exhibited room temperature ductility. Much more remains to be learned about ductility, fabricability, and strength of alloys in systems of this type. However, it appears from these preliminary tests that hydrogen absorption in tantalum and columbium can be significantly reduced by alloying.

CONCLUSIONS

An investigation of the compatibility of tantalum, columbium, and their alloys with hydrogen yielded the following conclusions:

1. Although solubility of hydrogen is less than 5 atomic percent in tantalum or columbium at temperatures from 1500° to 3000° F, extensive absorption of hydrogen (up to 38.2 at. % in tantalum and 47.5 at. % in columbium) occurred upon cooling at rates as high as 1500° F per minute from 3000° F.
2. Hydrogen present in solution or as a hydride embrittles both tantalum and columbium. The ductile-brittle bend transition temperature was increased from $<-320^{\circ}$ F for unalloyed columbium and tantalum to room temperature at a hydrogen content of 2 atomic

percent (220 ppm by weight) in columbium and 2 atomic percent (110 ppm by weight) in tantalum.

3. A screening study of 3 commercial tantalum alloys and 10 columbium alloys showed that all of these alloys reacted with hydrogen and exhibited embrittlement and disintegration similar to that observed for unalloyed tantalum and columbium.

4. Hydrogen absorption in tantalum and columbium can be reduced by alloying with rhenium to increase the electron-atom ratio. Hydrogen absorption was reduced to less than 1 atomic percent for alloys with an electron-atom ratio of 5.5 (25 at. % Re) or greater.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, April 29, 1966.

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